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<b>(54) Title:</b> BIODEGRADABLE POLYMERIC COMPOSITIONS COMPRISING STARCH AND A THERMOPLASTIC POLYMER		
<b>(57) Abstract</b>		
<p>Polymeric compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase, selected: A) from compositions comprising an agent with an interfacial effect selected from esters of polyols with mono- or polycarboxylic acids with dissociation constants within certain limits, the esters having specific values of the hydrophilic/lipophilic balance index HLB or being amongst the non-ionic surfactants which are soluble in water but cannot significantly be extracted by water from the compositions which contain them; B) from compositions wherein the thermoplastic polymer is an aliphatic or aliphatic-aromatic copolyester wherein the ratio (R) between the average viscometric molecular weight and the melt index is greater than 25,000 and C) from compositions wherein the thermoplastic polymer is selected from aliphatic-aromatic copolyesters, polyester-amides, polyester-ethers, polyester-ether-amides, polyester-urethanes and polyester-ureas and wherein the compositions are obtained by extrusion of the component maintaining a water content during the mixing stage from 1 to 5 % by weight.</p>		

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Biodegradable polymeric compositions comprising starch and a thermoplastic polymer

The present invention relates to biodegradable polymeric compositions with good resistance to ageing and to low humidities, comprising thermoplastic starch and a thermoplastic polymer incompatible with starch. In these compositions, starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase.

The invention relates in particular to biodegradable compositions which can maintain a high tear strength in conditions of low humidity.

It is known that the mechanical properties, particularly the tear strength, of products (films) produced from compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with starch in which the starch constitutes the dispersed phase undergo considerable deterioration because the starch gives up or absorbs water until it achieves equilibrium with the ambient humidity.

In conditions of relatively low humidity, for example 20% humidity, the material tends to become fragile since the dispersed phase becomes insufficiently plasticized because of the loss of water which raises the glass transition point above the ambient temperature.

In these conditions, when the starch particles constituting the dispersed phase are stressed they cannot deform and absorb the stress but remain rigid, thus initiating tearing.

Water is a very effective plasticizer of the starchy phase; however, it has the disadvantage that it is volatile and

that its concentration fluctuates in order to achieve equilibrium with the ambient humidity. High-boiling plasticizers such as glycerol, sorbitol, etherified or esterified sorbitol, ethylene glycol, trimethylol propane, pentaerythritol and polyols in general are therefore preferred.

Some of the water present during the plasticizing of the starch is supplied by the starch itself and some may be added.

Upon completion of the plasticizing and the mixing of the components, the water is removed by degassing to give a final content of about 1-3% by weight.

Water, like high-boiling plasticizers, modifies the viscosity of the starch phase and affects the rheological properties of the starch/polymer system, helping to determine the dimensions of the dispersed particles.

The most effective high-boiling plasticizers (glycerol in particular) tend to be lost from the system either because of evaporation in a ventilated atmosphere, particularly if the humidity undergoes cyclic variations, or by migration in contact with other hydrophilic materials such as cellulose.

In both cases, the concentration of plasticizer is no longer sufficient to keep the  $T_g$  of the dispersed phase below the temperature of use and the material becomes fragile.

To prevent this problem, plasticizers such as, for example, sorbitol, sorbitol mono-ethoxylate and trimethylol propane, which do not migrate and do not evaporate, have been used.

The effectiveness of these plasticizers, however, is quite low and the final characteristics of the material are worse than those obtained with the use of more effective plasticizers such as glycerol, particularly in conditions of low humidity.

To prevent the problems which arise in dry conditions, it has also been attempted to bring the  $T_g$  of the dispersed phase back to values below the temperature of use by increasing the quantity of high-boiling plasticizer. This gives rise to too soft a "feel" of the material when it is in the 50% relative humidity conditions in which the material is normally calibrated to achieve the maximum performance.

It has now unexpectedly been found that the problem of providing biodegradable heterophase compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with starch in which starch constitutes the dispersed phase and the polymer constitutes the continuous phase capable of maintaining high mechanical properties even in conditions of low relative humidity can be solved by using a composition selected from the following ones:

A) Compositions prepared by extrusion of the components in the presence of an interfacial agent selected from the group consisting of:

a) esters which have hydrophilic/lipophilic balance index values (HLB) greater than 8 and which are obtained from polyols and from mono- or polycarboxylic acids with dissociation constants  $pK$  lower than 4.5 (the value relates to the  $pK$  of the first carboxyl group in the case of polycarboxylic acids);

b) esters with HLB values of between 5.5 and 8, obtained from polyols and from mono- or polycarboxylic acids with less than 12 carbon atoms and with pK values greater than 4.5 (this value relating to the pK of the dissociation of the first carboxyl group in the case of polycarboxylic acids);

c) esters with HLB values lower than 5.5, obtained from polyols and from fatty acids with 12-22 carbon atoms, used in quantities of from 10 to 40% by weight relative to the starch;

d) non-ionic, water-soluble surfactants which, when added to the starch/thermoplastic polymer heterophase compositions indicated above, migrate in water by no more than 30% of their concentration after the material containing them has been immersed in water for 100 hours at ambient temperature;

e) reaction products of an aliphatic or aromatic diisocyanate with a polymer containing terminal groups reactive with the diisocyanates;

B) Compositions wherein the thermoplastic polymer incompatible with starch is a polyester comprising repeating units deriving from an aliphatic dicarboxylic acid and/or from a hydroxyacid with more than 2 carbon atoms and wherein the ratio R between the average viscosimetric molecular weight and the melt index of the polyester (measured at 180°C under a load of 5 kg) is greater than 25,000;

C) Compositions wherein the thermoplastic polymer incompatible with starch is a copolyester selected from the aliphatic-aromatic copolyesters, polyester-amides, polyester-ethers, polyester-ether-amides, polyester-ureas, and



polyester-urethanes, said compositions being obtained by extrusion of the components under conditions wherein the content of water during the extrusion mixing is maintained from 1 to 5% by weight as measured at the exit of the extruder, prior to conditioning.

The HLB index of the ester a) - c) of the A) compositions is given by the ratio between the molecular mass of the hydrophilic fraction of the molecule ( $M_h$ ) and the total molecular mass ( $M$ ) multiplied by 20:  $HLB = 20 \times (M_h/M)$ .

In the case of monoglycerides, the empirical formula normally adopted is the following:

$HLB = 20 (1 - S/A)$  in which  $S$  is the saponification number of the ester and  $A$  is the acidity number of the acid.

The hydrophilic/lipophilic balance of the esters is controlled by the length of the acid chain and by the number of hydroxyl groups which remain free after esterification.

The effect of the esters in bringing about compatibility in the case of starch/polyester systems is due to the interaction between the free alcohol groups of the ester and those of the starch and between the ester groups of the ester which brings about compatibility, and the polyester phase.

The esters of class a) are soluble in water; their effectiveness varies in dependence on the  $pK$  value of the acid and generally increases as the  $pK$  value decreases.

The best results are achieved with the esters of oxalic acid ( $pK = 1.23$ ), maleic acid ( $pK_1 = 1.83$ ), malonic acid

(pK<sub>1</sub> - 2.83), and mono-, di- and tri-chloroacetic acids (pK<sub>1</sub> 2.83, 1.48 and 0.70, respectively).

Mono- and di-esters of polyols containing 3 or more alcohol groups are preferred; mono- and di-glycerides, particularly of oxalic acid, are particularly preferred. Mono- and di-esters of sorbitol, trimethylol propane, pentaerythritol and similar polyols are also examples of compounds which can advantageously be used.

The esterification of the hydroxyl groups of the polyol is generally partial, affecting between 10 and 90% of the hydroxyl groups, preferably between 20 and 70%, and most preferably between 25 and 50%.

The partial esterification condition applies both to the esters a) and to the esters b) and c).

The esters a) are generally used in a ratio to the starch of from 1:30 to 1:2.5 by weight.

The quantities of the esters a) used are preferably from 5 - 40% relative to the starch, or from 0.5 to 20% by weight relative to the total composition. However, the compatibility effect starts to appear even at levels of 1-3% of the total weight of the composition.

The esters are generally used to replace 30-35% of the plasticizer; however, they may also be used without plasticizers.

The HLB values of some monoglycerides of class a) and the pK<sub>1</sub> and pK<sub>2</sub> constants of the corresponding acids are given by way of illustration:



Acid	pK1	pK2	HLB of the ester
Oxalic	1.23	4.19	12.4
Malonic	2.83	5.69	11.7
Succinic	4.16	5.61	11.1
Adipic	4.43	4.41	9.9
Pivalic	4.78	-	8.4

The effect of the esters of type a) in bringing about compatibility is such as to achieve a fine microstructure of the starch with a mean particle size at least one order of magnitude smaller than that of the particles of the compositions prepared, even in very favourable rheological conditions, in the absence of type a) agents for bringing about compatibility.

The average numeral size of the starch particles is between 0.1 and 0.5 microns and more than 80% of the particles have a size of less than 1 micron.

The water content of the compositions during the mixing of the components is preferably kept between 1 and 15% by weight.

It is, however, also possible to operate with a content of less than 1% by weight, in this case, starting with pre-dried and pre-plasticized starch.

The fine microstructure of the starch permits the production of a film which still retains good tensile and tear-strength properties after washing with water in order to remove the plasticizers. In these films, the small dimensions of the starch particles no longer enable tearing to be initiated.

The esters of classes b) and c) are insoluble in water and

are therefore not removed by washing.

Unlike the esters which are soluble in water and which, as well as acting as interfacial agents, also have a fairly good plasticizing effect, the insoluble esters, by virtue of the size of their hydrophobic aliphatic components, act mainly as interfacial agents, facilitating the slippage of the surfaces during stressing, thus minimizing the capacity of the particles, which have become rigid and no longer deformable as a result of loss of plasticizer, to initiate tearing.

Examples of esters of class b) are monoglycerides of caproic acid ( $pK = 4.85$ ;  $HLB = 7.3$ ), of suberic acid ( $pK_1 = 4.52$  and  $HLB = 6$ ) and of azelaic acid ( $pK_1 = 4.55$  and  $HLB = 5.8$ ).

Esters of caproic acid, particularly monoglycerides ( $HLB = 7.3$ ), are preferred since they can maintain a high tear strength of the films without detracting from their quality.

Esters b) are generally used in a ratio to the starch of from 1:30 to 1:2.5 or from 0.5 to 20% by weight relative to the total composition.

Examples of esters of class c) are monoglycerides of lauric acid ( $HLB = 5.4$ ) and of oleic acid ( $HLB = 4.2$ ). Examples of other monoglycerides which can be used are those of myristic, palmitic, stearic, erucic and linoleic acids.

The esters of class c), since materials of these types act as interfacial agents and not as lubricants, are used in high concentrations in comparison with those of the lubricants used in the prior art, that is, in concentra-

tions of from 3 to 10%, preferably from 5 to 10% by weight, which is equal to about 10-40% by weight relative to the starch.

Examples of non-ionic surfactants of class d) are alkoxyalted alkylphenols with HLB indices greater than 10, such as nonylphenol ethoxylate, with the degree of ethoxylation regulated in a manner such that the HLB is greater than 10.

The alkoxyalted alkylphenols are used in concentrations within a fairly narrow range, generally of from 3-7% of the weight of the composition. Concentrations outside this critical range have no effect. Other examples of surfactants of class d) are the ethoxylation products of sorbitol, starch, fatty acids, rosinic acid, tall oil, amides of fatty acids and ethanolamides.

The acids usable in the preparation of the esters a) to c) comprise saturated and unsaturated, linear or branched aliphatic and aromatic, mono- to polycarboxylic acids, possibly containing substituents selected, for example, from halogen atoms, hydroxyl groups, alkoxy groups, nitro groups, and ester groups, for example, acetyl citric acid.

Representative acids are:

formic acid, mono-, di- and tri-chloroacetic acid, propionic acid, butyric and isobutyric acids, amylic acid, isoamylic acid, pivalic acid and caproic acid, and fatty acids from lauric acid to docosanoic acid;

di-carboxylic acids such as oxalic, malonic, succinic, glutaric, adipic, suberic and azelaic acids;

hydroxy-acids such as glycolic, glyceric, lactic, citric,

tartaric, malic, and benzoic acids, substituted benzoic acid and salicylic acid.

The interfacial agents of class e) are preferably obtained by reaction of a diisocyanate such as hexamethylenediisocyanate with an aliphatic-aromatic polyester, such as polyepsilon-caprolactone. The agents e) are used in the amount of 1 to 10% by weight of the composition.

The polyols used for the preparation of esters a) to c) contain 3 or more carbon atoms and 2 or more alcohol groups, for example, glycerol, di- and polyglycerols, ethylene or propylene glycol, ethylene or propylene diglycol, polyethylene glycol, polypropylene glycol, 1,2-propandiol, trimethylol ethane, trimethylol propane, pentaerythritol, sorbitol, erythritol, xylitol, sucrose, 1,3-propandiol, 1,2-, 1,3-, 1,4-butandiol, 1,5-pentandiol, 1,6-, 1,5-hexandiol, 1,2,6-, 1,3,5-hexantriol, neopentyl glycol, and polyvinyl alcohol prepolymers.

These polyols as such or esterified with acids other than those used in the esters of classes a) and b) constitute an effective class of plasticizers usable in the compositions of the invention.

Polyols usable as plasticizers, in addition to those indicated above, comprise polyol acetates, ethoxylates and propoxylates, particularly sorbitol ethoxylate, glycerol ethoxylate, sorbitol acetate, and pentaerythritol acetate.

These and other polyols which may be used are described in USP 5,292,782.

The quantities of plasticizers used are generally from 1 to 100%, preferably from 10-30% by weight, relative to the

starch.

The thermoplastic polymers incompatible with starch usable in the A) type compositions of the invention are preferably selected from following groups of polymers:

- a) aliphatic polyesters obtained by polycondensation of hydroxy-acids with 2 or more carbon atoms or of the corresponding lactones or lactides. Examples of these polyesters and their derivatives are described in USP 5,412,005; polycaprolactones, hydroxy-butyric and hydroxyvaleric polymers and copolymers, polyalkylene tartrate, and glycolic and lactic acid polymers and copolymers are preferred;
- b) aliphatic polyesters obtained by polycondensation of diols with 2-10 carbon atoms with aliphatic dicarboxylic acids; polyalkylene succinate, polyalkylene adipate are preferred;
- c) aliphatic polycarbonates such as polyethylene carbonate and polypropylene carbonate, polyester-carbonates, polyamides-carbonates, polyesters amides-carbonates;
- d) esters of cellulose such as cellulose acetate, cellulose propionate, cellulose butyrate and mixed esters thereof;
- e) esters of starch such as starch acetate, propionate, and butyrate and starches esterified with acids up to C18; the degree of substitution of the starch is between 0.5 and 3;
- f) carboxymethyl cellulose, alkyl ethers and hydroxyalkyl ethers of cellulose, polysaccharides, chitin and chitosan, alginic acid and alginates;

g) vinyl esters and copolyesters both as such and partially hydrolyzed, such as polyvinyl acetate, polyvinyl acetate-/polyvinyl alcohol up to 50% hydrolysis, polyethylenevinyl acetate, polyethylene-acrylic acid and mixtures of polymers from a) to g).

The polyesters, particularly those obtained from hydroxy-acids, may be modified to form block copolymers or graft copolymers with polymers or copolymers which can react with the carboxyl and/or hydroxyl groups present in the polyesters.

The polymers and copolymers listed may be upgraded with chain extenders such as di- or polyisocyanates, di- or polyepoxides, or with polyfunctional compounds such as pyromellitic acid, pyromellitic anhydride.

The homopolymers and copolymers of epsilon-hydroxy-acids, particularly 6-hydroxy-caproic acid and the corresponding lactone are preferred.

The polyesters and their derivatives generally have melting points of between 40° and 175°C and molecular weights (weighted average) greater than 20000, preferably greater than 40000.

The polyesters and their derivatives can advantageously be used in mixtures with one or more polymers or copolymers obtained from ethylenically unsaturated monomers containing polar groups, preferably hydroxyl and carboxyl groups, such as ethylene/vinyl acetate, ethylene/vinyl alcohol and polyvinyl alcohol copolymers (the latter obtained by hydrolysis of polyvinyl acetate and ethylene vinyl acetate copolymers with degrees of hydrolysis of from 50 to 100%) and ethylene/acrylic acid copolymers.



The ethylene/vinyl alcohol copolymers preferably contain from 10 to 50% by weight of ethylene.

The alcohol groups of the polymers mentioned above may be converted into ether, ester, acetal or ketal groups.

Preferred mixtures contain poly-epsilon-caprolactone and ethylene/vinyl alcohol or ethylene/vinyl acetate or polyvinyl alcohol copolymers.

The ratio by weight between the polyesters and the polymers or copolymers containing alcohol groups is preferably between 1:30 and 30:1, more preferably between 1:15 and 15:1 and even more preferably between 1:6 and 6:1.

The ratio by weight between thermoplastic starch and e) - g) polymer is generally between 1:20 and 20:1 and preferably from 1:10 to 10:1, more preferably from 1:4 to 4:1 and is selected in a manner such that the polyester constitutes the continuous phase and the starch the dispersed phase.

Other preferred mixtures, used particularly in injection moulding, contain cellulose or starch esters with a degree of substitution of between 1 and 3, particularly cellulose acetate and starch acetate.

The thermoplastic starch present in the compositions is obtained from native starch extracted from vegetables such as potatoes, rice, tapioca, maize and/or from chemically or physically modified starch.

The compositions of the invention may include quantities of from 0.5 to 20% by weight of urea or hydroxides of alkali-earth metals, between 0.1 and 5% of inorganic salts of

alkali-metals or alkaline-earth metals, particularly LiCl, NaCl,  $\text{Na}_2\text{SO}_4$ , and also compounds containing boron, particularly boric acid, proteins and salts of proteins such as casein, gluten, caseinates, etc., abietic acid and derivatives thereof, rosinic acids, and natural gums.

Other hydrophobic polymers such as polyethylene, polypropylene and polystyrene and additives such as anti-oxidants, lubricants, flame-proofing agents, fungicides, herbicides, fertilizers and opacifiers, compounds with rodent-repellent effects, waxes and lubricants may be present.

The compositions are preferably prepared by mixing the components in an extruder heated to a temperature of between 100° and 220°C.

Instead of an extruder, the components may be mixed in any apparatus which can ensure temperature and shear stress conditions appropriate for the viscosity values of the thermoplastic starch and of the polymer incompatible with starch.

The starch may be treated to render it thermoplastic before being mixed with the other components of the composition or during the mixing of the components of the composition.

In both cases, known methods are used, with operating temperatures of between about 100° and 220°C, in the presence of plasticizers and possibly water.

The water content at the output of the extruder (that is, before any conditioning treatments) is preferably less than 5% by weight.

The content is regulated by degassing during extrusion or

with the use of dehydrated starch with a low water content.

The compositions of the invention are usable particularly in the preparation of films, sheets, fibres, in injection-moulding, thermoforming, coextrusion, and in the preparation of expanded materials.

Fields of use of particular interest are those of nappies and sanitary towels, of films for agriculture particularly for mulching, of bags, of films for cellophaning, of disposable articles, of expanded packaging elements, and of articles for nurserymen.

The films may be used in laminates with layers formed by polyesters, polyester-amides, polyamides, aliphatic polycarbonates, aromatic/aliphatic polycarbonates, soluble polymers such as polyvinyl alcohol or other polymers, with paper, and with layers of inorganic materials such as silica, aluminium, etc.

The compositions may be supplemented with fillers, preferably of natural origin, and with natural or modified resins such as abietic acid.

The compositions of group B) contain as peculiar components a polyester having a R ratio greater than 25,000 and preferably greater than 35,000 and more preferably comprised between 35,000 and 110,000. Polyesters with R ratios greater than 25,000 are preferably obtained by upgrading reaction, in the melt, of a polyester with a R ratio below 25,000 with a bi- or polyfunctional compound having groups which are reactive with terminal OH and/or COOH groups of the polyester. The quantity of the polyfunctional compound used is at least equivalent to the number of reactive groups of the polyester. The reaction is carried out until

the desired reduction of the melt index is achieved.

Representative polyfunctional compounds are di- and poly-isocyanates, epoxides and poly-epoxides, and the dianhydrides of tetracarboxylic acids.

Preferred compounds are di-isocyanates such as hexamethylene diisocyanate, dianhydrides of aromatic tetracarboxylic acids, and poly-epoxides.

The upgrading of the polyester can be obtained by extruding the polyester in the presence of the upgrading agent.

It is also possible to prepare polyesters having the desired melt-index and molecular-weight characteristics directly by polycondensation, as long as the viscosity values of the melt are not too high.

The polyesters usable for the preparation of the compositions of the invention are obtained from aliphatic polyesters comprising, in the chain, repeating units derived from an aliphatic dicarboxylic acid or from a hydroxy-acid with more than two carbon atoms.

The polyester are preferably selected from the same a) and b) groups of polyesters set forth for the A) type compositions.

The polyesters, particularly those obtained from hydroxy-acids, may be modified to form block copolymers or graft copolymers with polymers or copolymers which can react with the carboxyl and/or hydroxyl groups present in the polyesters.

The homopolymers and copolymers of epsilon-hydroxy-acids,

particularly 6-hydroxy-caproic acid and the corresponding lactone are preferred. The polycaprolactone preferably has a mean viscosimetric molecular weight greater than 100,000 and R-ratio values preferably of between 35,000 and 110,000.

The polyesters and their derivatives generally have melting points of between 40° and 175°C and molecular weights (viscosimetric mean) greater than 20,000, preferably greater than 40,000.

The polyesters and their derivatives can advantageously be used in mixtures with one or more polymers or copolymers obtained from ethylenically unsaturated monomers, containing polar groups, preferably hydroxyl and carboxyl groups, such as ethylene/vinyl acetate, ethylene/vinyl alcohol and polyvinyl alcohol copolymers (the latter obtained by hydrolysis of polyvinyl acetate and ethylene vinyl acetate copolymers with degrees of hydrolysis of from 50 to 100%) and ethylene/acrylic acid copolymers.

The ethylene/vinyl alcohol copolymers preferably contain from 10 to 50% by weight of ethylene.

The alcohol groups of the polymers mentioned above may be converted into ether, ester, acetal or ketal groups.

Preferred mixtures contain poly-epsilon-caprolactone and ethylene/vinyl alcohol or ethylene/vinyl acetate copolymers.

The ratio by weight between the polyesters and the polymers or copolymers containing alcohol groups is preferably between 1:6 and 6:1, more preferably between 1:4 and 4:1.

The ratio by weight between thermoplastic starch and polyester is generally between 1:10 and 10:1 and is selected in a manner such that the polyester constitutes the continuous phase and the starch the dispersed phase.

The compositions of the invention preferably comprise a plasticizer generally selected from polyols containing 3 or more carbon atoms and 2 or more alcohol groups such as glycerol, di- and polyglycerols, ethylene or propylene glycol, ethylene or propylene diglycol, polyethylene glycol, polypropylene glycol, 1,2-propandiol, trimethyl propane, pentaerythritol, sorbitol, erythritol, xylitol, sucrose, 1,3-propandiol, 1,2-, 1,3-, 1,4-butandiol, 1,5-pentandiol, 1,6-, 1,5-hexandiol, 1,2,6-, 1,3,5-hexantriol, neopentyl glycol.

The polyols indicated above may be used in the form of etherification or esterification products, such as polyol acetates, ethoxylates and propoxylates, particularly sorbitol ethoxylate, glycerol ethoxylate, sorbitol acetate, and pentaerythritol acetate.

The quantities of plasticizers used are generally from 1 to 100%, preferably from 10-30% by weight, relative to the starch.

The use of plasticizers of this type is described in USP 5,292,782, the description of which is incorporated herein, by reference.

The compositions may also comprise the interfacial agents described for the A) compositions. In this case, the use of the interfacial agent further improves the rheological characteristics of the compositions.



The thermoplastic starch present in the composition is obtained from native starch extracted from vegetables such as potatoes, rice, tapioca, maize and/or from chemically or physically modified starch.

The compositions of the invention may include quantities of from 0.5 to 20% by weight of urea or hydroxides of alkaline-earth metals, between 0.1 and 5% of inorganic salts of alkali-metals or alkaline-earth metals, particularly LiCl, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and also compounds containing boron, particularly boric acid, proteins such as casein, gluten, salts of proteins, abietic acid and derivatives thereof, rosinic acids, and natural gums.

Other hydrophobic polymers such as polyethylene, polypropylene and polystyrene and additives such as antioxidants, lubricants, flame-proofing agents, fungicides, herbicides, fertilizers and opacifiers, compounds with rodent-repellent effects, and waxes may be present.

The compositions are preferably prepared by mixing the components in an extruder heated to a temperature of between 100° and 220°C.

Instead of an extruder, the components may be mixed in any apparatus which can ensure temperature and shear-strain conditions corresponding to the viscosity values of the thermoplastic starch and of the polymer incompatible with starch.

The starch may be treated to render it thermoplastic before being mixed with the other components of the composition or during the mixing of the components of the composition.

In both cases, known methods are used, with operating

temperatures of between about 100° and 220°C, in the presence of plasticizers and possibly water.

The water content at the output of the extruder (that is, before any conditioning treatments) is preferably less than 5% by weight, and may be almost zero.

The content is regulated by degassing during extrusion or with the use of dehydrated starch with a low water content.

The use of polyesters having the molecular-weight and melt-index characteristics indicated above, possibly in combination with the agents with interfacial effect and a) and e) type used in A) compositions, gives rise to compositions which have a fine microstructure of the dispersed phase in which more than 80% of the particles have dimensions of less than 1 micron and the numeral average particle size is between 0.1 and 1 micron.

The B) compositions, similarly to the A) compositions, are usable particularly in the preparation of films, sheets, fibres, in injection-moulding, thermoforming, coextrusion, and in the preparation of expanded materials.

Fields of use of particular interest are those of nappies and sanitary towels, of films for agriculture, of bags, of films for cellophaning, of disposable articles, and of expanded packaging elements.

The films may be used in laminates with layers formed by polyesters, polyester-amides, polyamides, aliphatic polycarbonates, aromatic/aliphatic polycarbonates, soluble polymers such as polyvinyl alcohol or other polymers, with paper, or with layers of inorganic materials such as silica, aluminium, etc.

The compositions may be supplemented with fillers, preferably of natural origin, and with natural or modified resins such as abietic acid.

The C) compositions are characterised in that they comprise a polyester selected from the group consisting of aliphatic aromatic copolyesters, polyester-amides, polyester-ethers, polyester-ether-amides, polyester-urethanes and polyester-ureas, and in that they are obtained by extrusion under conditions wherein the content of water is maintained higher than 1% up to 5% by weight during the mixing of the components (content measured at the exit of the extruder i.e. prior to any conditioning treatment).

From the state of the art, particularly from WO93/07213 which describes compositions comprising starch and a copolyester obtained from mixtures of a terephthalic acid and adipic or glutaric acid and from an aliphatic diol, wherein the components are accurately dried, before being mixed, to a water content less than 1% wt. and from WO96/31561 which describes compositions comprising starch and copolyesters such as aliphatic-aromatic copolyesters, polyester-amides and polyester-urethanes, wherein starch is a plasticized product dried to a content of water less than 1% wt. or the copolyester-starch mixture is blended in the extruder under conditions to maintain the water content less than 1% wt, the expected result of mixing in the melt at high temperatures and in the presence of water at a level higher than 1% by weight a copolyester of the type above mentioned was a remarkable hydrolysis and degradation of the copolyester with consequent impairment of the properties of the final product.

Contrary to the expectations, it has been found that operating under the conditions used to prepare the composi-

tions C), the decrease of the molecular weight of the polyester is negligible.

It has further been found that, if the compatibilisation conditions during the mixing with extruder are good enough to obtain a dispersion of starch in form of particles having an average size less than 1 micron, preferably less than 0,5 micron, the resulting compositions present properties similar to those of polyethylene and which remain practically unchanged under relative low humidity conditions.

Another aspect which is characteristic of the compositions C) resides in that by extruding the compositions under the above specified humidity conditions i.e. a water content from 1 to 5% wt. it is possible to obtain products endowed with a microstructure finer than that obtainable by extruding, all the other conditions being the same, compositions wherein the polymeric hydrophobic component is a polyester totally aliphatic in its structure.

With the compositions C), the use of an interfacial agent as specified for the compositions A) and of a polymer with a molecular weight and melt index modified as set forth for the compositions B) is an optional condition.

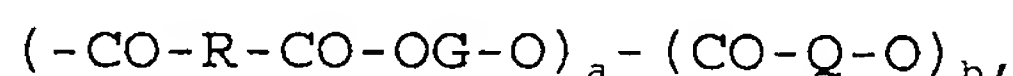
When the interfacial agent and/or the modified polymer is used, the rheological properties of the compositions are further improved.

The aliphatic-aromatic copolyesters preferably are of the random type. Block copolymers can also be used.

The copolyesters are obtained by polycondensation, according to known methods, of mixtures of an aliphatic

dicarboxilic acids such as adipic sebacic, succinic, azelaic or glutaric acids and/or a hydroxy acid with more than 2 carbon atoms or the corresponding lactone with an aromatic dicarboxilic acid such as terephthalic and isophthalic acids with a diol with 1-20 carbon atoms, such as 1,2-ethanediol, 1,3-propandiol, 1,4-butanediol, 1,4-cyclohexandimethylol.

The copolyesters have in general formula:



wherein up to about 40% by mols of R is a bivalent non-aromatic radical  $\text{C}_1\text{-C}_{12}$  and the remaining of R is a p-phenylene radical; G is up to 30% by mols a radical selected from  $-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2$ ,  $-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2$  the remaining of G being an ether-polyalkylenic radical with molecular weight higher than 250 or a radical  $(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_4$ ; Q derives from a hydroxyacid with more than 2 carbon atoms; a) and b) are molar fractions of the polymer with a) being comprised from 0.6 and 1 and b) from 0 to 0,4.

Copolyesters of the above type are described in US 5,446,0-79 and WO 93/07123 which are herein incorporated by reference.

The polyester-amides have in general a structure deriving for 30-70% by weight from an aromatic or aliphatic-aromatic ester and from 70-30% from an aliphatic amide.

Examples of polyester-amides are poly-epsilon-caprolactone-epsilon-caprolactam, poly-alkylenadipate-epsilon-caprolactam.

Examples of usable polyester-amides are described in EP-A-

641817 and in WO96/21689, WO-96/21690, WO-96/21691 and WO-96/21692, the description of which is herewith incorporated by reference.

The polyester-ether copolymers can be obtained from an aromatic dicarboxylic acid such as terephthalic acid and a polyalkylenoxide.

The polyester-urethane and polyester-urea copolymers can be obtained according to known methods; for instance the polyester-urethanes from a dicarboxylic acids such as terephthalic acid and an aliphatic diisocyanate.

The compositions C) comprise from 20 to 95% by weight of starch and 5-80% by weight of copolyester. Preferably the content of starch is from 30 to 75% by weight.

The copolyesters can be used in mixtures with the polymers and copolymers containing polar groups as specified for the compositions A) and B).

The weight ratio between the copolyester and the (CO) polymer containing polar groups is the same as specified for A) and B) compositions.

The thermoplastic starch present in the compositions is obtained from native starch or chemically or physically modified starch as described for the compositions B). The compositions preferably contain a plasticizer of the type as specified in the compositions A) and B) with amounts therein disclosed.

The compositions may contain additives as set forth for the compositions A) and B).



The composition are prepared by extrusion of the components under conditions that the content of water during the mixing stage is maintained, by degassing, at values from 1 to 5% by weight.

The content of water of the native starch can be comprised from 1 to 16% by weight.

The extrusion conditions (temperature which can range from 100° to 220°C and shearing forces) are selected as to obtain a good compatibilisation between starch and the incompatible copolyester.

The starch may be treated to render it thermoplastic according to the known method e.g. operating in the presence of plasticizers and water, before being mixed with the components of the composition or during the mixing.

The compositions are useful for the same applications, as disclosed for the compositions A) and B).

Thanks to the rather high melting point of the copolyester used in the compositions C), the same are particularly usable in applications wherein a food thermal resistance is required.

The following examples 1-45 (examples 1, 42 and 44 are comparison examples) are provided by way of non-limiting illustration of A) compositions of the invention, examples 1A-6A and comparative examples 1A-2A by way of non-limiting illustration of B) compositions; and examples 1B and 2B of C) compositions.

The esters used in the examples 1-45 were prepared in accordance with conventional methods. In the case of the

stronger carboxylic acids, the use of acid catalysts was not necessary but it sufficed to remove the water produced by the reaction. For the weaker acids, particularly the fatty acids, the reaction was catalyzed with small amounts of toluene sulphonic acid.

Since the esterification did not affect all of the hydroxyl groups of the polyol (so that both ester functions and alcohol functions were present simultaneously in the reaction product) but only a fraction of between 10 and 90% of the hydroxyl groups, preferably between 20 and 70%, and more preferably between 25 and 50%, it was possible to continue the reaction until the acid was used up. Any traces of unreacted acid could be neutralized with organic or inorganic bases, preferably triethanolamine.

The product of these partial esterifications was constituted predominantly by the polyol with the desired degree of esterification; the second largest fraction was constituted by unsubstituted polyol, and the remainder was constituted by polyol with higher degrees of substitution or, in the case of dicarboxylic acids, by oligomeric forms.

The inherent viscosity given in the examples 1A-6A is expressed by the equation:

$$[\eta]_{inh} = \frac{[\eta]t/t^{\circ}}{c}$$

where:

$t^{\circ}$  = time taken by a known volume of pure solvent to pass through the capillary of the viscosimeter;

$t$  = time taken by an identical volume of the solution

containing the polymer to pass through the capillary,  
 $c$  = concentration of the polymer in the solution, expressed  
in g/dl.

The instrument used for the measurements was a Bischoff  
viscosimeter.

The measurement was carried out in tetrahydrofuran at 25°  
with the use of 1g of polymer in 100ml of solvent.

In the following examples all "parts" are intended by  
weight, unless otherwise stated.

#### EXAMPLE 1 (comparison)

A composition containing 55 parts of PCL TONE 787 (Union  
Carbide), 31 parts of Globe maize starch 03401 (Cerestar),  
0.25 parts of erucamide, 12 parts of glycerol, and 1.75  
parts of water was mixed in an OMC single-screw extruder  $D$   
= 20 mm and  $L/D$  = 30 with an operating temperature profile  
of 80/180/150/130°C at 70 rpm.

The pellets obtained were then supplied to a Haake single-  
screw extruder,  $D$  = 19 mm and  $L/D$  = 20, with a film-forming  
head.

The heating profile during the blow-moulding was 115/120/125/130°C at 30 rpm.

The film obtained constituted the reference material.

#### EXAMPLES 2-40

The compositions given in the following table were mixed and filmed with the use of the method of Example 1 and with the PCL, starch, water and erucamide parts remaining the same but with all or some of the glycerol replaced by the esters indicated below:

Table 1

Example	2	3	4	5	6	7	8	9	10	11	12	13
glycerol	9	9	9	6	9	6	5	5	5	6	6	6
chloro- acetate	3											
tri-chloro- acetate		3										
pivalate			3	6			2	3				
caproate					3	6	5	4				
1,5 caproate									6			
laurate										6		
S-oleate											3	
S-oleate												6

Example	14	15	16	17	18	19	20	21	22	23	24	25
glycerol	11	9	7	-	4	2	9	6	9	9	-	6
sorbilene					4	4						
oxalate	1	3	5	12	4	6						1
S-oxalate							3	6				
TMP-oxalate									3			
EG-oxalate										3	12	
caproate												5

Example	26	27	28	29	30	31	32	33	34	35	36	37
glycerol	9	6	-	9	9	-	9	5	7	9	9	6
malonate	3	6	12									
maleate				3								
succinate					3	12						
adipate							3					
azelate								7				
suberate									7			
acetyl citrate										3		
oleate											3	6

Example		38	39	40
glycerol		6	9	6
nonylphenol 10		6		
nonylphenol 19			3	6

## NOTE

Glycerol and sorbilene are polyols used as plasticizers; sorbilene is a sorbitol monoethoxylate.

Unless expressly indicated, the ester was obtained by the reaction of a COOH function with one mole of glycerol.

caproate 1,5 resulted from the reaction of 1.5 moles of caproic acid per mole of glycerol

S-oleate was monosorbitane oleate

S-oxalate was produced from one mole of oxalic acid and two moles of sorbitol

TMP-oxalate was produced from one mole of oxalic acid and two moles of trimethylol propane

EG-oxalate was produced from one mole of oxalic acid and two moles of ethylene glycol

nonylphenol 10 was nonylphenol ethoxylate with 10 moles of ethylene oxide; HLB=13

nonylphenol 19 was nonylphenol ethoxylate with 19 moles of ethylene oxide; HLB=16



EVALUATION OF THE MATERIAL SAMPLES

The films were conditioned at 20°C and 15% RH for 48 hours and were then subjected to preliminary tear-strength screening. The evaluation was carried out manually and the appraisal was as follows:

Example	very good	good	poor	very poor
1				x
2	x			
3	x			
4			x	
5		x		
6			x	
7		x		
8		x		
9		x		
10		x		
11		x		
12		x		
13		x		
14	x			
15	x			
16	x			
17	x			
18	x			
19	x			
20	x			
21	x			
22	x			
23	x			
24	x			
25	x			
26		x		
27	x			
28	x			
29			x	
30		x		
31	x			
32		x		
33		x		
34		x		
35			x	
36			x	
37		x		
38		x		
39			x	
40		x		

PAPER CONTACT TEST

The formulations which gave good or very good responses in the preliminary screening were tested in terms of tear strength after the corresponding films had been placed between sheets of pure cellulose paper at 50°C and RH < 10% for two months.

In this case, preliminary manual screening was again carried out.

The test was quite severe since the paper was able to take plasticizers such as glycerol from the films.

The results were as follows:

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Example	very good	good	poor	very poor
1				x
2		x		
3		x		
5		x		
7		x		
8		x		
9		x		
10		x		
11		x		
12		x		
13		x		
14		x		
15	x			
16	x			
17	x			
18	x			
19	x			
20		x		
21		x		
22		x		
23		x		
24	x			
25		x		
26		x		
27	x			
28	x			
30		x		
31	x			
32			x	
33		x		
34		x		
37		x		
38		x		
40		x		

TEAR STRENGTH AFTER THE FILMS HAD BEEN WASHED IN WATER

This was the most severe test since the conventional plasticizers (glycerol and sorbilene in this case) as well as the water-soluble esters were completely removed.

In practice, the film was immersed in distilled water for 24 hours, after which it was left to dry for 25 hours at ambient temperature.

The films which were good or very good in the paper contact test were subjected to this test; evaluation was again manual.

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Example	very good	good	poor	very poor
1				x
2		x		
3		x		
5		x		
7		x		
8		x		
9		x		
10			x	
11			x	
12			x	
13			x	
14			x	
15		x		
16	x			
17	x			
18	x			
19	x			
20		x		
21	x			
22			x	
23			x	
24	x			
25		x		
26			x	
27		x		
28	x			
30		x		
31		x		
33			x	
34			x	
37		x		
38		x		
40		x		

MECHANICAL PROPERTIES

The mechanical properties of some films subjected to washing with water are given in comparison with the untreated films.

Example No.	Sigma b MPa	Ext.* %	Modulus MPa	Breaking energy KJ/m <sup>2</sup>
1 untr.	33	849	200	6837
1 washed	19	3	1179	16
7 untr.	12	684	156	3958
7 washed	8	314	752	1790
12 untr.	22	969	271	6409
12 washed	12	8	751	45
13 untr.	23	946	161	6340
13 washed	11	326	573	1768
17 untr.	33	923	170	7515
17 washed	19	490	885	4750
18 untr.	33	849	200	6837
18 washed	19	420	996	4970
19 untr.	26	741	170	5042
19 washed	17	393	1007	3339
36 untr.	25	1076	156	7582
36 washed	10	9	804	38
37 untr.	23	946	161	6349
37 washed	6	326	546	1768

\* Ext. = elongation at break

Example 41

A composition containing 55 parts of PCL Tone 787, 31 parts of Globe maize starch 03401 (Cerestar), 6 parts of oxalic acid monoglyceride, 3 parts of glycerol, and 5 parts of sorbitol monoethoxylate was mixed in an extruder as in Example 1 and then filmed. The film was then subjected to the water washing test. The tensile properties, compared with the same film which had not been washed, were as follows:

	Sigma b	Ext.	Modulus	Breaking energy
	MPa	%	MPa	KJ/m <sup>2</sup>
untr. film	28	760	234	6321
washed film	23	733	310	5870

Example 42 (comparison)

A composition containing 44 parts of cellulose acetate with a degree of substitution DS = 2.5, 16 parts of diacetin, 32.8 parts of maize starch, 0.2 parts of erucamide and 8 parts of Sorbilene was mixed in a 30 mm APV-2030 XLT extruder with two screws and L/D = 35+5. The heating profile was as follows: 60/100/180 x 14°C and RPM=170.

The extruded material was pelletized and was pressure moulded at 190°C to give test pieces 2 mm thick. A test piece was broken cold in order to investigate the fracture surface.



Example 43

Using the method of Example 42, a similar composition was prepared but with the Sorbilene replaced by oxalic acid monoglyceride. The material was pressure moulded as in Example 42.

The mechanical properties compared were as follows:

		Example 42	Example 43
Sigma b	MPa	22	20
Ext.	%	6.6	6.6
Modulus	MPa	2231	2121
Breaking energy	KJ/m <sup>2</sup>	67.7	69.4
MFI	g/10'	0.17	4.65
Spiral	cm	557	900

As can be seen, the use of the ester considerably fluidized the composition in both MFI and spiral terms, for given tensile properties. The effect in bringing about compatibility was even clearer from SEM morphological analysis of the fracture surfaces, from a comparison of which, the material containing the ester was clearly more homogeneous.

MFI was measured at 170°C with a load of 5 kg.

Example 44 (comparison)

A composition exactly the same as that of Example 1 except that the PCL was replaced by a random aliphatic-aromatic copolyester obtained from 60:40 butylene adipate/butylene terephthalate was prepared with the use of the method described in Example 1.

The material was filmed and characterized.

Example 45

Example 44 was repeated with the introduction of 5 parts of malonic acid monoglyceride instead of the same quantity of glycerol.

The material was filmed and characterized.

The tensile properties compared were as follows:

		Example 44	Example 45
Sigma b	MPa	6	22
Ext.	%	408	788
Modulus	MPa	91	79
Breaking energy	KJ/m <sup>2</sup>	1432	3780

Comparative Example 1A

200g of epsilon-caprolactone, 3.8 mg of tin octanoate, and 186 mg of 1,4 butandiol were loaded into a 300ml glass reactor and heated to 180°C for 24 hours with stirring and in an atmosphere of nitrogen.

The polymer obtained has the following characteristics:

Inherent viscosity	1.42 dl/g
MW (viscosimetric)	125000
MI	5.0

Example 1A

Comparative example 1A was repeated but with 105mg of 1,4 butandiol instead of 186mg.

The polymer obtained had the following characteristics:

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Inherent viscosity	1.75 dl/g
MW (viscosimetric)	183000
MI	1.8

## Example 2A

253.3g of Union Carbide PCL Tone 787, dried under vacuum at 50°C for 24 hours, was placed in a 800ml glass reactor and heated to 180°C with stirring (100 RPM).

When the temperature had been reached, 1.0 ml of 1,5 hexamethylene di-isocyanate was added and the reaction was continued for two hours.

The characteristics of the starting PCL and of the reaction product were as follows:

	PCL Tone 787	Example 2A
Inherent viscosity	1.28 dl/g	1.38 dl/g
MW (viscosimetric)	108000	121000
MI	7.0	2.5

## Example 3A

A composition containing 99.8 parts of PCL Tone 787, dried as in Example 2A, and 0.4 parts of 1,6-hexamethylene di-isocyanate was supplied to an OMC twin screw extruder, L/D=36 and D=60mm, operating under the following conditions:

- temperature profile: 20/90/90/140/175/190x4/170/150°C
- flow-rate: 10 kg/h
- RPM: 150

The extruded and pelletized material had the following

characteristics:

Inherent viscosity	1.35 dl/h
MW (viscosimetric)	118000
MI	2.9

Examples 4A-6A, Comparative Example 2A

The following compositions:

Example	2A(comp)	4A	5A	6A
PCL Example 1A (comp)	49%	-	-	-
PCL " 1A	-	49%	-	-
PCL " 2A	-	-	49%	-
PCL " 3A	-	-	-	49%
Maize starch	36	36	36	36
Glycerol	12	12	12	12
Water	3	3	3	3

were mixed in an OMC single-screw extruder L/D=30 and D=20mm operating with a 80/180/150/130 temperature profile at 70 RPM.

The pellets obtained were then supplied to a Haake single-screw extruder, L/D=20 and D=19mm with a filming head; the temperature profile during the blow-moulding was 115/120/1-25/130 and the RPM = 30.

The films obtained, which were about 40 microns thick, were characterized from the point of view of their tensile properties and of their tear strength. The measurements were made with test samples conditioned at 50% and 20% RH. In particular, with regard to the tear strength, measurements were made at both low and high speed; in the first case, an Instron instrument was used with a speed of 250

mm/min, in accordance with ASTM D-1938; in the second case an Elmendorf pendulum was used in accordance with ASTM-1922.

Example	2Acomp.		4A		5A		6A	
Sigma b (MPa)	10	20	10	18	9	18	10	18
Ext. (%)	830	185	820	530	595	535	605	570
Elas. Modulus (MPa)	205	975	235	780	135	735	170	710
Breaking energy (MJ/m <sup>3</sup> )	83	30	91	91	107	116	97	94
Tear strength 1 (N/mm)	97	83	89	85	87	90	87	85
Tear strength 2 (N/mm)	200	7	150	150	180	128	170	135

Tear strength 1 = low speed

Tear strength 2 = high speed

For each example, the data for 50% and 20% relative humidity are given (with 50% in the first column).

#### Example 1B

54 parts of a Eastman Chemical 14766 copolyester (based on terephthalic acid, adipic acid and butandiol), 33.4 parts of maize starch Cerestar Globe 03401, 5.8 parts glycerol and 6.5 parts water were fed to a twin-single screw extruder APV V30 mod. 2030 operating under the following conditions:

- standard screws (residence time 80 seconds);
- screw diameter: 30 mm
- L/D: 10
- RPM: 1790
- Thermal profile: 60/100/180 x 14°C
- Active degassing

The obtained pellets had water content of 1.18% by weight.

Upon having removed the starch by solubilization with HCl 5 M, the average numerical dimensions of the dispersed starch phase was determined by SEM and was comprised within

0.3 and 0.5  $\mu\text{m}$ .

The intrinsic viscosity of the polyester, recovered by extraction with  $\text{CHCl}_3$ , was:

$[\eta] = 0.86 \text{ dl/g}$  in  $\text{CHCl}_3$  at  $30^\circ\text{C}$  against  $[\eta] = 0.93 \text{ dl/g}$  of the starting polymer.

The pellets were subjected to film blowing in a Haake singlescrew extruder, having a diameter of 19 mm,  $L/D = 20$  at  $140^\circ\text{C}$ , thereby to obtain a film having a thickness of about 45  $\mu\text{m}$ .

The mechanical properties of the obtained films are shown in the following table:

$\sigma_y$	$\epsilon_y$	$\sigma_b$	$\epsilon_b$	Mod	Energy
Mpa	%	Mpa	%	Mpa	KJ/m <sup>2</sup>
5.7	9.1	7.4	478	161	1566

#### Example 2B

Example 1B was repeated by substituting the standard screws by screws including back mixing (reverse) sections. In this case, the residence time in the extruder was raised to 130 seconds.

The pellets were examined according to Example 1B and the following results were obtained:

Water: 1.76% by weight

Particle dimensions comprised within 0.3 and 0.4  $\mu\text{m}$

Polyester viscosity after blending:  $[\eta] = 0.83 \text{ dl/g}$

The pellets were subjected to film blowing according to

Example 1B.

The mechanical properties of the films were the following:

	$\sigma_y$	$\epsilon_y$	$\sigma_b$	$\epsilon_b$	Mod	Energy
	Mpa	%	Mpa	%	Mpa	KJ/m <sup>2</sup>
Film as such	7.3	13.5	12.6	784	154	3476
Washed film (*)	9.0	14.6	6.7	550	198	2501

(\*) the plasticizers were removed from the film by emulsion in water for 24 hours

The same washed film, conditioned at 23°C and 20% RH, had a tear strength of 139 KJ/m<sup>2</sup> at a speed of 1 m/sec.

The pellets were finally processed in an extruder having a flat head to obtain a sheet having a thickness of 6000  $\mu\text{m}$ ; the sheet was found suitable for thermoforming.



CLAIMS

1. Biodegradable heterophase polymeric compositions having good resistance to ageing and to low humidity conditions, comprising thermoplastic starch and a thermoplastic polymer incompatible with starch, in which starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase, selected from:

A) compositions containing an interfacial agent selected from the following classes of compounds:

a) esters of polyols with mono- or polycarboxylic acids with values of the dissociation constant pK lower than 4.5 (the value relates to the pK of the first carboxyl group in the case of polycarboxylic acids), characterised by hydrophilic/lipophilic balance index values (HLB) greater than 8;

b) esters of polyols with mono- or polycarboxylic acids with less than 12 carbon atoms and with pK values greater than 4.5 and having HLB indices between 5.5 and 8;

c) esters of polyols with C<sub>12</sub>-C<sub>22</sub> fatty acids having HLB indices lower than 5.5, the esters being used in quantities of from 10 to 40% by weight of the starch;

d) non-ionic, water-soluble surfactants which, when added to the starch/thermoplastic polymer compositions indicated above, migrate in water by no more than 30% wt of their concentration after the material containing them has been immersed in water for 100 hours at ambient temperature,

e) reaction products of an aliphatic or aromatic diisocyanate with a polymer containing terminal groups reactive with the diisocyanates;

B) compositions wherein the thermoplastic polymer incompatible with starch is a polyester comprising repeating units deriving from hydroxyacids with more than 2 carbon atoms and/or from aliphatic dicarboxylic acids, and in which the ratio R between the average viscosimetric molecular weight and the melt index (measured at 180°C under a 5 kg load) is

greater than 25,000.

C) compositions wherein the thermoplastic polymer incompatible with starch is selected from the group consisting of aliphatic-aromatic copolyesters, polyester-amides, polyester-ethers, polyester-ether-amides, polyester-urethanes and polyester-ureas, said compositions being obtained by extrusion under conditions wherein the content of water during the mixing of the components is maintained from 1 to 5% by weight (content measured at the exit of the extruder, prior to any conditioning).

2. A composition according to Claim 1, wherein the composition is selected from the group A) compositions and wherein the esters are obtained from polyols containing 3 or more carbon atoms and 2 or more alcohol groups.

3. Compositions according to Claim 2 in which the polyol is glycerol.

4. Compositions according to Claims 2 or 3 in which the esters are monoglycerides.

5. Compositions according to preceding Claims 2-4, in which the ester a) is an ester of oxalic, malonic, succinic, adipic, glutaric, maleic, citric, tartaric, lactic, or mono-, di-, or tri-chloroacetic acid.

6. Compositions according to Claim 5 in which the ester a) is (on average) the monoglyceride.

7. Compositions according to Claims 2-4, in which the ester b) is obtained from caproic, suberic, or azelaic acid.

8. A composition according to Claim 7 in which the ester

is, on average, the monoglyceride.

9. Compositions according to Claims 2-4, in which the ester c) is, on average, the monoglyceride of lauric or oleic acid.

10. Compositions according to Claim 2, in which the surfactant d) is selected from alkoxylated substituted alkyl phenols with HLB indices greater than 10.

11. Compositions according to the preceding claims 2 to 10 in which the ratio by weight between the thermoplastic starch and the thermoplastic polymer incompatible with starch is such that the starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase.

12. Compositions according to preceding Claims 2-9 in which the quantities of the esters a) and b) used are from 0.5 to 20% by weight relative to the total composition.

13. Compositions according to the preceding claims 2 to 12, comprising a plasticizer.

14. Compositions according to Claim 13, in which the plasticizer is selected from polyols with 3 or more carbon atoms and with 2 or more alcohol groups, the polyols possibly being etherified or esterified.

15. Compositions according to Claim 14, in which the polyol is selected from glycerol, sorbitol, etherified or esterified sorbitol, ethylene glycol, and trimethylol propane.

16. Compositions according to Claims 12 to 15, in which a quantity of plasticizer of from 1 to 100% by weight

relative to the starch is used.

17. Compositions according to Claim 16, in which the ester a) or b) is used in a ratio of from 1:30 to 1:2.5 by-weight to the starch.

18. Compositions and materials according to the preceding claims, in which the thermoplastic polymer is selected from aliphatic or aliphatic-aromatic polyesters obtained by polycondensation of hydroxy-acids with 2 or more carbon atoms, or from the corresponding lactones or lactides, or by polycondensation of a diol with 1-12 carbon atoms with a dicarboxylic aliphatic acid or with mixtures thereof with dicarboxylic aromatic acids.

19. Compositions according to Claim 18 in which the polymer is a poly-epsilon-caprolactone.

20. A composition according to Claim 1, wherein the composition is selected from the group B) compositions and the R ratio is between 40,000 and 110,000.

21. Compositions according to Claim 20, in which the polyester is the product of the polycondensation of an aliphatic dicarboxylic acid with a diol with 2 or more carbon atoms, or the polycondensation product of an aliphatic hydroxy-acid with more than 2 carbon atoms or of a lactone or lactide thereof.

22. A composition according to Claim 21, in which the polyester contains units derived from an aromatic dicarboxylic acid and/or from a mixture of aliphatic dicarboxylic acids or of hydroxy-acids.

23. Compositions according to preceding Claims 21-22, in

which the polyester is poly-epsilon-caprolactone, poly-epsilon-caprolactone/epsilon-caprolactam, poly-epsilon-caprolactam/butylene adipate.

24. Compositions according to Claim 23, in which the polycaprolactone has a mean viscometric molecular weight greater than 100000 and a R ratio of between 40,000 and 110,000.

25. Compositions according to the preceding claims 21-24 comprising a plasticiser selected from polyols with 3 or more carbon atoms.

26. Compositions according to Claim 25, in which the polyol is selected from glycerol, sorbitol, trimethylol propane and pentaerythritol.

27. Compositions according to Claims 25 and 26, in which the quantity of polyol used is from 10 to 100% relative to the starch.

28. A composition according to Claim 1, wherein the composition is selected from the group C) compositions, and wherein the starch is dispersed in the copolyester matrix in the form of particles having average numeral dimension less than 1  $\mu\text{m}$ .

29. Compositions according to claim 28, wherein the starch particles have average numeral dimension less than 0.5  $\mu\text{m}$  and more than 70% of the particles have dimension less than 0,5  $\mu\text{m}$ .

30. Compositions according to claims 28-29 wherein the copolyester is obtained by polycondensation of mixtures of dicarboxilic aromatic and aliphatic acids with an aliphatic

C<sub>2</sub>-C<sub>20</sub> diol.

31. Compositions according to Claim 30, wherein the aliphatic dicarboxylic acid is selected from the group consisting of adipic, glutaric and sebacic acids and the aromatic acid is terephthalic acid.

32. Compositions according to Claims 28-30, wherein the copolyester is obtained by polycondensation of an aliphatic C<sub>2</sub>-C<sub>20</sub> diol with a mixture of a hydroxyacid with more than 2 carbon atoms or the corresponding lactone with terephthalic acid.

33. Compositions according to claims 28-32, wherein the copolyester is selected from the group consisting of polyalkylen adipate-polyalkyleneterephthalate, polyalkylen-adipate-polyalkylenisophthalate and polyalkylensebacate - polyalkyleneterephthalate.

34. Compositions according to claims 28-33 wherein the content of units having an aliphatic structure is comprised from 30 to 70% by mols.

35. Compositions according to claim 28 wherein the copolyester-amide is selected from the group consisting of poly-epsilon-caprolactone-epsilon-caprolactam, poly-alkylenadipate-epsilon-caprolactam and polyalkylenesuccinate- epsilon-caprolactam.

36. Compositions according to claims 26 to 35, wherein the content of starch is comprised from 5 to 95% by weight and the content of the copolyester is from 95 to 5% by weight.

37. Compositions according to claims 28 to 36 comprising a plasticiser selected from the group consisting of glycerol,

sorbitol, polyglycerol, esters and ethers of glycerol, sorbitol and polyglycerol; 1,3-propandiol and pentaerythritol.

38. Compositions according to claims 28 to 37 comprising a polymer selected from an aliphatic polyester, cellulose acetates, ethylene-vinylalcohol copolymers, ethylene-vinylacetate copolymer and polyvinylalcohol in an amount up to 30% by weight of the composition.

39. Process for preparing a composition according to the preceding claims 28 to 38, comprising extruding the components of the composition under conditions wherein the content of water is maintained from 1 to 5% by weight during the mixing of the components.

40. A film obtained from the compositions from claims 28-38.

41. Use of the films according to claim 40 in the manufacture of nappies, of sanitary towels, of bags and of laminated paper.

42. Use of the films according to claim 40 in the agricultural field for mulching application.

43. Use of the compositions of claims from 28 to 39 for the manufacture of expanded molded articles usable in packaging, and of disposable articles.

44. Films obtained from the compositions A) and B) of claim 1 or from the compositions of claims 2 to 27.

45. Use of the film according to Claim 44 in the manufacture of nappies, of sanitary towels, of bags, of laminated paper, of laminates, and of films treated with inorganic



products such as silica and aluminium.

46. Use of the films of Claims 44 in the agricultural field and for cellophaning.

47. Use of the compositions A) and B) of claim 1 and of the compositions of the preceding claims 2 to 27 for the manufacture of expanded materials usable in packaging, and of disposable articles.

48. A material produced from heterophase compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase, characterized by a microstructure of the dispersed phase in which at least 80% of the particles have dimensions smaller than 1  $\mu\text{m}$ .

49. A material according to Claim 48 in which the average numeral particle size is between 0.1 and 0.5  $\mu\text{m}$ .

50. A material according to Claim 48 and 49 in film form.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP97/06103 <b>(22) International Filing Date:</b> 5 November 1997 (05.11.97)  <b>(30) Priority Data:</b> TO96A000890      5 November 1996 (05.11.96)      IT TO96A000996      9 December 1996 (09.12.96)      IT  <b>(71) Applicant (for all designated States except US):</b> NOVAMONT S.P.A. [IT/IT]; Via Fauser, 8, I-28100 Novara (IT).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BASTIOLI, Catia [IT/IT]; Via della Noce, 63, I-28100 Novara (IT). BELLOTTI, Vittorio [IT/IT]; Via Mora e Gibin, 9, I-28010 Fontaneto d'Agogna (IT). CELLA, Gian, Domenico [IT/IT]; Via Minghetti, 1, I-28100 Novara (IT). DEL GIUDICE, Luciano [IT/IT]; Piazzale Siena, 4, I-20146 Milano (IT). MONTINO, Sandro [IT/IT]; Via Bellotti, 15, I-27038 Robbio Lomellina (IT). PEREGO, Gabriele [IT/IT]; Via Voghera, 20, I-20144 Milano (IT).  <b>(74) Agents:</b> RAMBELLI, Paolo et al.; Jacobacci & Perani S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <b>(88) Date of publication of the international search report:</b> 6 August 1998 (06.08.98)
<b>(54) Title:</b> BIODEGRADABLE POLYMERIC COMPOSITIONS COMPRISING STARCH AND A THERMOPLASTIC POLYMER  <b>(57) Abstract</b> <p>Polymeric compositions comprising thermoplastic starch and a thermoplastic polymer incompatible with starch, in which the starch constitutes the dispersed phase and the thermoplastic polymer constitutes the continuous phase, selected: A) from compositions comprising an agent with an interfacial effect selected from esters of polyols with mono- or polycarboxylic acids with dissociation constants within certain limits, the esters having specific values of the hydrophilic/lipophilic balance index HLB or being amongst the non-ionic surfactants which are soluble in water but cannot significantly be extracted by water from the compositions which contain them; B) from compositions wherein the thermoplastic polymer is an aliphatic or aliphatic-aromatic copolyester wherein the ratio (R) between the average viscometric molecular weight and the melt index is greater than 25,000 and C) from compositions wherein the thermoplastic polymer is selected from aliphatic-aromatic copolyesters, polyester-amides, polyester-ethers, polyester-ether-amides, polyester-urethanes and polyester-ureas and wherein the compositions are obtained by extrusion of the component maintaining a water content during the mixing stage from 1 to 5 % by weight.</p>		

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/06103

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6    C08L67/02    C08L67/04    C08L3/00    C08J5/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6    C08L    C08J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 24447 A (MICHIGAN STATE UNIVERSITY) 14 September 1995  see page 4, line 11 - line 26 see page 5, line 25 - line 30 see page 7, line 25 - line 32 see page 19, line 21 - line 35 ---	1,2,11, 13-16, 18,19, 44-47
X	EP 0 596 437 A (FLUNTERA AG) 11 May 1994  see page 16, line 26 --- <div style="text-align: center;">-/--</div>	1-4,11, 13-16, 18,19, 44-47
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
° Special categories of cited documents :  <div style="display: flex;"> <div style="flex: 1;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-size: 1.2em;">5 March 1998</div>		Date of mailing of the international search report  <div style="text-align: center; font-size: 1.5em; font-weight: bold;">12. 06.98</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-size: 1.2em;">Andriollo, G</div>

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PCT/EP 97/06103

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 19680 A (NOVAMONT SPA) 12 November 1992 cited in the application see page 16, paragraph 2 - paragraph 3 & US 5 412 005 A (BASTIOLI ET AL.) ---	1
A	WO 93 00399 A (PROCTER & GAMBLE) 7 January 1993 ---	1
A	EP 0 516 030 A (EMS-INVENTA) 2 December 1992 -----	1

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 97/06103

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9524447 A	14-09-95	US 5500465 A CA 2183772 A EP 0749460 A JP 9505107 T	19-03-96 14-09-95 27-12-96 20-05-97
-----			
EP 0596437 A	11-05-94	DE 4237535 A AT 158805 T BR 9304477 A CN 1088226 A DE 9321391 U DE 59307460 D ES 2107600 T	11-05-94 15-10-97 26-07-94 22-06-94 25-09-97 06-11-97 01-12-97
-----			
WO 9219680 A	12-11-92	EP 0525245 A IT 1245485 B IT 1256693 B IT 1263114 B AT 155161 T AU 658180 B AU 1650992 A AU 658207 B AU 2058292 A BR 9205258 A CA 2074649 A CA 2084994 A CN 1071588 A DE 9219021 U DE 69220754 D DE 69220754 T DE 539541 T DK 539541 T EP 0539541 A ES 2103943 T FI 925978 A JP 5228205 A JP 2527523 B JP 6502676 T KR 9608112 B RU 2095379 C SK 390192 A	03-02-93 20-09-94 12-12-95 30-07-96 15-07-97 06-04-95 21-12-92 06-04-95 04-02-93 27-07-93 02-02-93 04-11-92 05-05-93 27-02-97 14-08-97 04-12-97 30-01-97 15-09-97 05-05-93 01-10-97 31-12-92 07-09-93 28-08-96 24-03-94 20-06-96 10-11-97 07-12-94

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 97/06103

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 9219680 A		RU 2089151 C	10-09-97	
		US 5286770 A	15-02-94	
		US 5412005 A	02-05-95	
		AT 127034 T	15-09-95	
		DE 69204351 D	05-10-95	
		DE 69204351 T	11-04-96	
		DK 512360 T	18-09-95	
		EP 0512360 A	11-11-92	
		ES 2077280 T	16-11-95	
		JP 5123550 A	21-05-93	
		US 5534150 A	09-07-96	
		AT 165385 T	15-05-98	
		CN 1077966 A	03-11-93	
		DE 69318058 D	28-05-98	
		EP 0560244 A	15-09-93	
		IL 104942 A	10-06-97	
		JP 6041351 A	15-02-94	
		US 5462980 A	31-10-95	
	-----			
	WO 9300399 A	07-01-93	AU 670914 B	08-08-96
AU 2251492 A			25-01-93	
BR 9206215 A			02-05-95	
CZ 9302882 A			13-07-94	
EP 0591409 A			13-04-94	
FI 935820 A			04-02-94	
HU 67772 A			28-04-95	
JP 6508868 T			06-10-94	
MX 9203308 A			01-12-92	
NO 934808 A			25-02-94	
PL 173320 B			27-02-98	
PT 8542 U			31-03-93	
PT 101726 A,B			31-01-96	
SK 147693 A			07-09-94	
US 5422387 A			06-06-95	
-----				
EP 516030 A	02-12-92	DE 4117628 A	17-12-92	
		AU 643385 B	11-11-93	
		AU 1715592 A	17-12-92	
		CA 2070041 A	30-11-92	
		DE 59207696 D	30-01-97	



### Information on patent family members

PCT/EP 97/06103

Patent document  
cited in search report

Publication date

Patent family member(s)

Publication date

EP 516030 A

JP	2006839	C
JP	5200822	A
JP	7025118	B
NZ	242921	A
US	5316578	A

11-01-96  
10-08-93  
22-03-95  
27-04-94  
31-05-94

1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377
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